FINAL REPORT:

High-Altitude NO and NO_y Measurements Using a New, Lightweight Chemiluminescence Instrument (NCC2-786)

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Abstract

Field measurements of NO and NO_y were proposed, using a new lightweight dual-channel NO/NO_y instrument to investigate processes regulating NOx, NO_y and ozone in the lower and middle stratosphere. The measurements were intended to be part of the HSRP 1994 field program and to complement ER-2 measurements planned for the Airborne Southern Hemisphere Ozone Experiment (ASHOE). Altitudes above the operational envelope of the ER-2 were targeted, in the tropics and middle latitudes. A fully operational 35 kg instrument was planned, to be tested in the stratosphere and incorporated into a lightweight payload with ClO, BrO, ozone, T and P and a tracer instrument (probably a tunable diode laser spectrometer currently under development) on the Perseus A.

Progress and Results

The proposed stratospheric flight instrument was to measure NO using chemiluminescence and NO_y by catalytic conversion to NO followed by chemiluminescence. The instrument was designed, components and sub-assemblies were extensively tested, but it has not flown because Perseus A did not emerge, nor did any other RPA platform.

During the development we performed extensive laboratory studies aimed at optimizing the detection methods and undertook detailed investigations to characterize the NO_y catalytic conversion process over a broad range of conditions (including those relevant to the current controversy surrounding tropospheric NO_y measurements). We also made significant progress in developing alternative detection schemes.

1. NO Chemiluminescence Detection

We fabricated and tested several new designs for the chemiluminescence cell. The final design has a higher sensitivity, lower zero artifact (in the lab), and lower weight (by a factor of 5) than previous cells. Kinetic modeling of the chemiluminescence cell was undertaken, allowing optimization of the detector performance within the power and gas-consumption constraints applicable to a range of operational scenarios.

2. NO_y Catalytic Conversion

Using the NO_y species NO, NO_2, HNO_3, and isopropyl nitrate and the potential interferences HCN, CH_3CN, NH_3, and N_2O conversion efficiencies as a function of reducing-agent concentration with both H_2 and CO; (c) the effect of humidity and O_3 on conversion efficiency; (d) loss of NO in the catalyst; and (e) the efficacy and suitability as catalytic converters (or inlets) of 24 k gold, 18 k gold, gold doped with 1% cobalt, silver, platinum, stainless steel, and quartz. The most significant results were the discovery of a gas-phase process that contributes to the conversion of HNO_3 to NO and the identification of conditions that produce oxidizing sites on/in the catalyst, allowing HCN, CH_3CN, and NH_3 to be converted to NO with high efficiency. We have submitted a manuscript for publication that provides a detailed description of these measurements and discusses their implications for in situ measurement of atmospheric NO_y (including recommendations for performing measurements using catalytic conversion).

3. Directions for the Future

Laser-induced fluorescence (LIF) is a highly sensitive and specific spectroscopic technique for detection of a number of small molecules, including NO. The size, weight, complexity, and power requirements of existing laser systems used to generate the required UV radiation have prevented LIF from being widely applied to field measurements. In collaboration with Lew Goldberg of the Naval Research Laboratory in Washington, DC, we investigated using semiconductor lasers to power a compact, lightweight, electrically efficient (low power consumption, low heat generation), solid-state, inexpensive sources of tunable, narrow-bandwidth UV radiation to be used for LIF. We frequency- quadrupled the output of a high-power diode laser to generate tunable light near 215 nm, the wavelength required for NO LIF. These pilot studies have been published and led to the submission of a patent application. We recently received a grant from the NSF to continue this research.

Publications and Patents

1. D.A.V. Kliner, B.C. Daube, J.D. Burley, and S.C. Wofsy, Laboratory Investigation of the Catalytic Reduction Technique for Measurement of Atmospheric NO_y, J. Geophys. Res. (in press, 1996).

2. L. Goldberg and D.A.V. Kliner, Deep-UV Generation by Frequency Quadrupling of a High-Power GaAlAs Semiconductor Laser, Opt. Lett. 20, 1145 (1995).

3. L. Goldberg, D.A.V. Kliner, and J.P. Koplow, Solid-State Laser Source of Tunable Narrow-Bandwidth Ultraviolet Radiation, U.S. Patent Application (submitted, Feb. 1, 1996).